PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 2002P2127W 01	**FOR FURTHER ACTION**	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/EP 03/07139	International filing date *(day/month/year)* 03.07.2003	Priority date *(day/month/year)* 09.07.2002
International Patent Classification (IPC) or both national classification and IPC C23C28/02		
Applicant SIEMENS AKTIENGESELLSCHAFT et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 10 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 2 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the opinion
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
08.10.2003	26.07.2004
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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP 03/07139

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

Description, Pages

1-9 as originally filed

Claims, Numbers

1-11 received on 26.04.2004 with letter of 23.04.2004

Drawings, Sheets

1/1 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).

   ☐ the language of publication of the international application (under Rule 48.3(b)).

   ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   ☐ contained in the international application in written form.

   ☐ filed together with the international application in computer readable form.

   ☐ furnished subsequently to this Authority in written form.

   ☐ furnished subsequently to this Authority in computer readable form.

   ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   ☐ the description, pages:

   ☐ the claims, Nos.:

   ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-11
	No:	Claims	
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-11
Industrial applicability (IA)	Yes:	Claims	1-11
	No:	Claims	

2. Citations and explanations

   see separate sheet

Re Item I
Basis of the report

Claim 1 in its present form does not meet the requirements of Article 34(2)(b), because from the original disclosure and the original claim 1 it was clear that the outer layer is also a MCrAlY layer. However, according to claim 1 presently on file the outer layer only consists of the elements Co, Cr, Al and Ni.
Therefore the examination is carried out as if originally filed claim 8 would not have been incorporated into claim 1.

Re Item II
Priority

The priority of the subject-matter of claims 10 and 11 is not valid, since this subject-matter is not found in the original disclosure.

Re Item V
Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. The following documents are referred to in this communication; the numbering will be adhered to in the rest of the procedure:

D1: US-A-5 507 623 (KOJIMA YOSHITAKA ET AL) 16 April 1996 (1996-04-16)
D2: WO 99 55527 A (SIEMENS AG ;STAMM WERNER (DE)) 4 November 1999 (1999-11-04)
D3: MUELLER G ET AL: 'OXIDE SCALE GROWTH ON MCRALY COATINGS AFTER PULSED ELECTRON BEAM TREATMENT' SURFACE AND COATINGS TECHNOLOGY, ELSEVIER, AMSTERDAM, NL, vol. 108/109, no. 1-3, 1998, pages 43-47, XP001004819 ISSN: 0257-8972
D4: US-A-4 615 864 (DARDI LOUIS E ET AL) 7 October 1986 (1986-10-07)
D5: US-A-6 001 492 (JACKSON MELVIN ROBERT ET AL) 14 December 1999 (1999-12-14)

2.

2.1. The present application focuses on the protection of parts, which require a high oxidation resistance, such as blades or vanes of gas turbines. As an object it is stated "to describe a protective layer [i.e. layer between the substrate and the thermal barrier coating] with a good oxidation resistance and good bonding to the thermal barrier coating" (page 2, line 30 - 34).

2.2. To solve the problem it is suggested that the protective layer consists of two layers, an inner conventional MCrAlY layer and an outer MCrAlY layer having a different composition and being characterized in having a γ-Ni phase and an Al content of up tp 6.5 %.

3. Prior art, novelty and inventive step.

3.1. D1 describes a turbine blade, which is coated and in contact with a first layer consisting of MCrAlY, with M = Co or Ni/Co. A second layer is applied on the first layer, the second layer consisting of MCrAlY, with M = Ni (abstract, claims 1, 8). Compositions for both layers are disclosed, for example, in col. 4, line 42 - 64 and claim 15, having an Al concentration in the second layer, i.e. the outer layer, from 5 - 15 %. Test specimen No. 9, 10, 19 and 20 (Table 1) have Al contents of the outer layer of 4 and 5 wt. % and a composition of the intermediate layer falling into the one of claim 1 of the present application.
Claim 1 does not exclude that the outer layer zone has a gradient in its composition, like the upper layer of D1. Hence, it is understood that the Al content of up to 6.5 wt. % concerns the average Al content of the outer layer zone. In addition, in D1 the two layers are first deposited and then heat treated to effect diffusion (col. 8, line 34 - 64), which means that before heat treatment both layers have a homogenous profile of composition.
Hence, the only feature of claim 1 of the present application, which is not explicitly mentioned, is that the outer layer has the structure of γ-Ni.
However, in col. 3, line 29 - 32, it is taught that in the Ni-Cr-Al system there is a γ- and a ß-phase and that it is difficult to reduce the ß-phase by a slight change in the Al content. Also from what follows in col. 3, line 33 - 41, it is evident that the ß-phase is not desired. Hence, from D1 alone it becomes clear that it is desired to have predominately γ-phase in the MCrAlY layers.
Claim 1 is novel with respect to D1, because D1 does not teach the complete absence

of the ß-phase, i.e. to have the γ-phase only in the outer MCrAlY layer, as it is done by claim 1. However, claim 1 is not inventive with respect to D1, because it is obvious from D1 to try to reduce the ß-phase as much as possible and to have, in the most desirable case, only the γ-phase.
D1 further teaches to add one or more of the elements Ta, Zr, Ce to the outer layer (col. 6, line 37 - 47). In Example 1, a test specimen is prepared from a substrate made from an alloy comprising 5 wt. % Ti. After the MCrAlY layers are applied the specimen is finally heated at 1060°C for 4 h. It must be assumed that under these conditions a significant amount of Ti diffuses into the MCrAlY layers.
Therefore, also claims 2, 6, 8 and 9 are not inventive with respect to D1.

3.2. D2 teaches a product of manufacture, especially a gas turbine blade, which has a metallic base with a corrosion resistant layer, which consists of a first and a second MCrAlY layer, the first MCrAlY layer being contiguous with the base. The second MCrAlY layer mainly consists of the γ-phase (abstract). Preferably, the second layer is remelted by e- or ion beam to result in an outer layer consisting of a pure outer γ-phase. It is also possible to use galvanic methods to obtain a second layer being in the γ-phase (page 8, line 20, - page 9, line 27).
Therefore, D2 differs from claim 1 of the present application in that the composition of the intermediate layer is specified differently and that the lowest Al content of the outer MCrAlY layer is 7 wt. %, whereas in the present application 6.5 wt. % is the maximum Al content.
It is taught that, if the MCrAlY layer is in the γ-phase, a thin and stable α-Al_2O_3 film is formed already at the beginning of the oxidation. This results in a good adhesion of the thermal barrier layer, which is coated on top of the Al_2O_3, to the MCrAlY layer and, further, also to an increased life-time of the thermal barrier layer, because spallation is reduced. In opposition to that the α-Al_2O_3 layer is thicker and its growth rate faster for a MCrAlY layer which is in the ß-phase, which results in a higher spallation rate (page 5, line 23, - page 25, page 11, line 23 - 35). Hence, D2 clearly teaches the advantages of the MCrAlY being in the γ-phase and ideally consisting only of the γ-phase for improving oxidation resistance and bonding to the thermal barrier coating. These, however, are also the technical problems, which the present application wishes to overcome.

3.3. Paper D3 teaches a pulsed electron beam treatment method which improves the oxidation resistance of MCrAlY coatings (abstract). Table 3 shows that before treatment a ß- and a γ-phase can be found, whereas after the treatment there is almost only pure γ-phase present.

3.4. Therefore, for the skilled artisan, the teachings of D2 and D3 affirm what was already expressed by D1, namely to try to achieve an outer MCrAlY layer, which consists of a pure γ-phase.

3.5. The skilled artisan who is looking to improve further the protective coating of D1, would consult the teaching of D2 of how to make outer MCrAlY layers having a pure γ-phase.
D2 teaches alloying components, like Re, Si, Hf, Ta, Zr (page 5, line 1 - 5) and especially Re is emphasized to have a concentration between 0 - 20, 1 - 20 or 5 - 11 wt. % (page 7, line 11 - 15, claim 5). Further, the MCrAlY layer contains Cr (claim 4). It also discloses that the outer MCrAlY layer may be thinner than the inner MCrAlY layer (page 7, line 1 - 4).
Hence, claims 4 and 5 are not inventive with respect to the combination of D1 and D2. The smaller amount of Re, like in claim 10 of the present application, is considered as a selection, which does not involve an inventive step, because no surprising technical effects over D2 are taught in the present application connected with the claimed range for the Re content.

3.6. Finally, D4 discloses an alloy for coating of superalloys, which provides good oxidation and thermal fatigue resistance (abstract), for example, to components used in gas turbines (col. 1, line 24 - 29). In col. 5, line 4 - 7, it is contemplated to apply the composition as the outer layer of a coating system consisting of two MCrAlY layers. Although the claimed compositions (col. 3, line 27 - 38, claim 1) contain Mn as a mandatory constituent also coating compositions are taught which are particularly useful to provide oxidation resistance. These include 10 - 35 wt. % Cr, 5 - 15 wt. % Al and the balance being Fe, Co or Ni, for example a Ni base alloy containing 5 - 35 wt. % Co. Cr may also lay in the range of 15 - 40 wt. %, if the Al content is low, i.e. 3 - 13 wt. % (col. 4, line 5 - 17). These compositions fall into or strongly overlap with the one claimed in claim 7 of the instant application.

3.7. The skilled person, who is looking to improve the protection layer of D1 will apply all measures which are taught in the state of the art and providing these improvements. Therefore, besides trying to achieve an outer layer consisting of the γ-phase only, he will also contemplate about alloy compositions for the outer layer, which have the best oxidation resistances. Therefore, he will apply MCrAlY alloys in the outer layer, which have the compositions taught in D4. On one hand, this will result in outer layers containing Mn, and hence laying out of the scope of claim 7. On the other hand, the skilled person will also use the compositions taught in col. 4, line 5 - 17, falling fully or

partly into those claimed by claim 7. Therefore, this claim is not considered to be inventive.

3.8. A continuously graded interface (claim 3) is not inventive for the following reasoning:
In D1 the outer layer already has a gradient in Al, Cr and Ni concentration of the outer layer. It is said, that the gradient in Al reduces thermal damage (col. 5, line 43 - 61).
D5 discloses a thermal barrier coating for use in turbines, combustors and the like, which has a graded layer between the substrate and the thermal-insulating layer 12. The innermost layer may be made of MCrAl or MCrAlY; the adjacent layer also contains a Cr phase, while the outermost layer contains a Cr and a Pt phase. (col. 4, line 6 - 24). These three layers may be discrete but are, more generally, three successive regions of a continuously graded structure (col. 3, line 35 - 45). The idea in providing a graded structure is to provide graded thermal expansion properties, which moderate the transition between the metal substrate and the thermal insulating ceramic layer. This is said to result in a coating system which is highly resistant to spallation. (col. 3, line 11 - 22).
Hence, the skilled person seeking for further improvement of the bond coating of D1 would consider the teaching of D5, i.e. to reduce spallation rate by adapting the thermal expansion properties of the substrate and the thermal insulating coating via a graded bond layer. This would result in an MCrAlY bond layer with a graded concentration of the constituents.

3.9. Also claim 11 is not inventive. Heat treatment of an MCrAlY layer prior to application of a thermal barrier coating is known in the art (D2, page 8, line 20, - page 9, line 17, and D3). This treatment results in a remelting but also in the formation of thermally grown oxide, mostly aluminum oxide. An oxide can only be formed, if small quantities of oxygen are present. The amounts of oxygen listed in claim 1 are considered to constitute such small quantities.

Re Item VII
Certain defects in the international application

The application does not meet the provisions of Rule 5.1.a.ii PCT, because the most relevant prior art, e.g. Documents D1 - D5, are not cited and briefly discussed.

Re Item VIII
Certain observations on the international application

Clarity.

1. Parts of the description (Summary of the invention" and page 5, line 5 ff.) teach to apply an outer layer, which has a ß-NiAl structure instead of an MCrAlY layer having a γ-Ni phase structure. However, such a layer is no claimed, and is, hence, not a subject of the invention. Therefore, the respective paragraphs of the description concerning such a letter need to be omitted.

2. Claim 1 is not supported by the description in that its wording is different from what is taught on pages 2, line 30, - page 3, line 17. The subject-matter of the independent claims should be identical with what is taught in the part of the description usually referred to as "Summary of the Invention".
Claim 1 lacks further the essential technical feature that the outer MCrAlY layer shows at a temperature of 900 - 1100°C a pure γ-Ni matrix (page 6, line 31 - 34).
In addition, there is a clear contradiction between what is said on page 3, line 16 - 17, and what is claimed: Claim 1 reads that the protective layer **consists of** an intermediate MCrAlY layer zone and an outer layer zone, i.e. two distinct layers, and not a single layer or a plurality of layers.
Lack of clarity also arises from the fact that in claim 1 the outer layer has the composition consisting of Co, Cr, Al and Ni, whereas according to the description it is a modified MCrAlY layer, which means, that it mandatorily contains Y (see also item I, above).
Finally, the intermediate MCrAlY layer is defined in claim 1, line 9 - 10, such that M = Co, whereas according to line 19 and 20 M may be one of Co, Fe, Ni.

3. Claim 6: How can the yttrium being added and/or be partially replaced? Further it is unclear what is meant with "or the outer zone".

4. Claim 7 is out of the scope of claim 1, on which it depends, because the claimed composition does not contain Y.

5. Page 4, line 27 - 30, is unclear. What is meant by: **A part of Y or in addition this MCrAlY layer zone 16** can also contain Hf, Zr, La, Ce or another Lanthanide? A part of

Y always contains Y.

claims

1. Highly oxidation resistant component (1),
having a substrate (4),
a protective layer (17),
which consists of
an intermediate MCrAlY layer zone (16) on or near the substrate (4),
which has the composition (in wt%): 10% - 50% Co, 10% - 40% Cr, 6% - 15% Al, 0,02% - 0,5% Y, Ni base,
and an outer layer zone (19)
which has the structure of the phase γ-Ni and has a content of Aluminum of up to 6.5wt% and
consists of pure γ-Ni phase and
which has the composition (in wt%): 15 - 40% Cr, 5 - 80% Co, 3 - 6.5% Al and Ni base,
wherein the outer layer zone (19) is onto the intermediate MCrAlY layer zone (16),
wherein M is at least one element out of the group Co, Fe, Ni.

2. Component according to claim 1,
wherein the protective layer (17) consists of two separated layers (16, 19).

3. Component according to claim 1,
with a continuously graded concentration of the composition of the intermediate and outer zone (16, 19) inside the protective layer (17).

4. Component according to claim 1,
wherein the outer layer zone (19) is thinner than the intermediate layer (16) on or near the substrate (4).

5. Component according to claim 1, wherein the intermediate MCrAlY-layer (16) or the outer layer zone (19) contains at least one further element such as (in wt%): 0,1% - 2% Si, 0,2% - 8% Ta or 0,2% - 5% Re.

6. Component according to claim 1, wherein the Yttrium of MCrAlY of the intermediate MCrAlY zone (16) or the outer zone (19) is added and/or at least partly replaced by at least one element out of the group Hf, Zr, La, Ce and/or other elements of the Lanthanide group.

7. Component according to claim 1, wherein the outer layer (19) zone has the composition (in wt%): 20 - 30% Cr, 10 - 30% Co, 5 - 6% Al and Ni base.

8. Component according to claim 1, wherein the MCrAlY layer zone (16, 19) contains Ti (Titanium) and/or Sc (Scandium).

9. Component according to claim 1, wherein on the outer layer zone (19) a thermal barrier coating (13) is formed.

10. Component according to claim 5, wherein the rhenium content (Re) is between 0.2 and 2wt%.

11. Component according to claim 9, wherein a heat treatment prior to applying a thermal barrier coating is carried out in an atmosphere with a low oxygen partial pressure, especially at 10^{-7} and 10^{-15} bar.